Environ Geol (2009) 58:833–841
DOI 10.1007/s00254-008-1559-7

ORIGINAL ARTICLE

Phosphorus in suspended matter and sediments of a hypertrophic lake. A case study: Lake Dianchi, China

Hu Jun · Liu Jiantong · Liu Yongding

Received: 1 June 2008 / Accepted: 17 September 2008 / Published online: 7 October 2008

Abstract From June 2004 to December 2004, Lake Dianchi, which had large scale of cyanobacterial blooms was investigated in order to study P-fractionation in the suspended matter and the sediment. The investigation improves our understanding of phosphorus in Lake Dianchi and the relationship between phosphorus and cyanobacterial blooms. It contributes to the available literature on the behavior of P in hypertrophic lakes. The distribution of P-fractions in Lake Dianchi was not uniform from northwest to south, but was closely related to the trophic status of the whole lake. The concentrations of total phosphorus, labile P (NH_4Cl-P), Organic P (NaOH-NRP) and loss on ignition in suspended matter were positively correlated with the strength of cyanobacterial blooms. Total phosphorus in suspended matter was relatively stable for almost half an year and closely related to Chl. *a* concentration. The main content of organic phosphorus is in the cyanobacterial blooms. The concentrations of phosphorus bound to metal oxides and carbonates (NaOH-SRP and HCl-P) in sediment were similar to NaOH-SRP and HCl-P in the corresponding suspended matter. The latter two forms of P in suspended matter were not affected by cyanobacterial blooms, indicating that the inorganic phosphorus is derived from the sediment after resuspension from the sediment due to wind and wave action. The contribution of the different P-fractions to TP in sediment and in suspended matter indicates that NH_4Cl-P in the suspended matter is an important buffer for maintaining dissolved phosphorus in water.

Keywords Phosphorus · Suspended matter · Sediment · Fractionation · Cyanobacterial bloom · Lake Dianchi

Introduction

Nutrient pollution is the main cause of eutrophication of lakes. High nutrient levels cause rapid growth of algae that become blooms, which endanger public health and healthy aquatic ecosystems. Among the nutrient elements, phosphorus is the primary nutrient limiting algae growth in lakes. Phosphorus in lakes is basically present in two forms: (1) soluble P that is available for uptake by the algae and particulate P either already in the algae or associated with abiotic particulate matter and (2) suspended particles that mainly consist of inorganic matter and organic matter including living organisms plus organic detritus. The particles are derived from the lake sediment or an external source. In shallow lakes wind-induced turbulence appears to have a big influence on the exchange between sediment and water and it can increase the suspension of sediment particles and even promote the outward movement of phosphorus dissolved in pore water. Deeper lakes can also be significantly influenced by Seiche-induced resuspension (Gloor et al. 1994; Pierson and Weyhenmeyer 1994). Besides lakes, there have been the studies on P-resuspension in rivers (Chase and Sayles 1980; Quilbe et al. 2006). Phosphorus reaching the bottom of lakes can be recycled into the water column, creating water quality problems long even after external inputs have been eliminated. The release of phosphorus from the sediment to lake water occurs either as the mobilization of phosphorus from

H. Jun
Instiue of Hydroecology, Ministry of Water Resources & Chinese Academy of Sciences, Wuhan, China
e-mail: xhujun@gmail.com

L. Jiantong (✉) · L. Yongding
Instiue of Hydrobiology, Chinese Academy of Sciences, Wuhan, China
e-mail: jtliu@ihb.ac.cn

suspended sediment particles or after mobilization into the dissolved P-pool in sediment pore water and the subsequent upward transport of the dissolved species into the water column (Boström et al. 1988). The present trophic status of lakes is usually dependent on the P-concentration in the water, while the future trophic status, can be greatly influenced by the phosphorus content of lake sediments (Hu et al. 2006; Hu et al. 2007; Kaiserli et al. 2002). At the present time, it is the pollution caused by internal phosphorus loading that is attracting attention (Rydin 2000; Van der Molen et al. 1998).

In this paper, Lake Dianchi, a hypereutrophic shallow lake was selected for the study of phosphorus in a whole lake using the technique of P-fractionation. Lake Dianchi is suffering from severe cyanobacterial blooms, and the water blooms mainly composed by cyanobacterial species and the percentage sometimes reaches to 100%(Li et al. 2005; Wang et al. 2008). Because the water and sediment in Lake Dianchi has already been investigated (Fang et al. 2004; Hu et al. 2007), the spatio-temporal changes of suspended matter were given more attention in this study. The samples of suspended matter and sediment were collected simultaneously to examine P-fractions; the intention being to study the relationship between suspended-P and algae blooms and to improve our knowledge on the spatio-temporal-distribution of phosphorus in the whole Lake Dianchi.

Materials and methods

Study area

Lake Dianchi (24°40′–25°02′ N, 102°36′–103°40′E) located in Yunnan-Guizhou plateau, is the sixth largest fresh water highland lake in China. It has a surface area of about 300 km^2 and maximum and mean depths of 10 and 4.4 m respectively. In recent years a cyanobacterial bloom in the whole lake occurs annually. According to the investigation undertaken in 2002, Lake Dianchi has become a hypereutrophic lake (Fang et al. 2004). The parameters showing water characteristics of Lake Dianchi are listed in Table 1 and the distribution plots of the total phosphorus (TP), chlorophyll *a* (Chl. *a*) and the trophic status index (TSI) are shown in Fig. 1 (Fang et al. 2004).

Sampling and analysis

The eight sampling sites (Fig. 2) were established by GPS navigation from north to south in the central of Lake Dianchi so as to avoid the disturbance of the lakeshore. Surface sediment samples (0–2 cm) were collected by KC sediment core sampler (Denmark). At the same time, the water samples were collected from the surface and from 2 m below the surface. The sediment samples and water samples were placed into separate air-sealed plastic bags and cleaned 1 L bottles, respectively. All the samples were kept in the portable refrigerator and delivered to the laboratory. They were stored at 4°C until analyzed. Samples were collected at bimonthly intervals from June to December 2004.

Sediment samples were homogenized and divided into subsample. The suspended matter in lake water was separated by filtering the water samples through pre-combusted GF/F filters (Whatman) of known weight. The sediment subsamples and the suspended matter captured in filters were used to make a sequential analysis of water content and organic matter, which are determined as weight loss after drying at 80°C and loss on ignition (LOI) at 550°C (Baldock and Skjemstad 1999; Hazelton and Murphy 1992). LOI was expressed as a percentage of dry weight. The filters with suspended matter were used to determine the concentration of Chl. *a* (APHA 1995) in μg/L. Every sediment subsample ignited at 550°C was further used to analyze TP according to the literature (Paludan and Jensen 1995). TP of suspended matter was calculated as the difference between TP of the unfiltered water sample and TP of the filtered water sample. The fractionation in the remaining sediment subsamples and the suspended matter captured in filters was performed according to a sequential

Table 1 The water quality 2001–2002

	pH	T (°C)	COD[a]	SD(cm)	DO	Chl. *a*	TN	NH_3-N	TP	TDP	DP
North-west	8.81	17.56	14.59	44.6	8.38	149	4.45	0.69	0.317	0.053	0.033
North	8.57	17.09	12.72	54.7	7.89	78	2.66	0.42	0.142	0.025	0.012
Middle	8.52	17.47	11.63	64.1	7.18	57	2.26	0.39	0.118	0.023	0.012
South	8.77	17.13	11.11	62.3	7.78	52	2.14	0.41	0.124	0.025	0.012

Each parameter is the mean value of the sample sites in each area. For the demarcation of each of the four areas, refer to Fig. 2

TP, TN, TDP, DP and DO were expressed in mg/L. Chl. *a* was expressed in μg/L

TP total phosphorus (mg/L), *TN* total nitrogen, *TDP* total dissolved phosphorus, *DP* dissolved phosphorus, *SD* Secchi disk transparenc

[a] Analyzed by $KMnO_4$

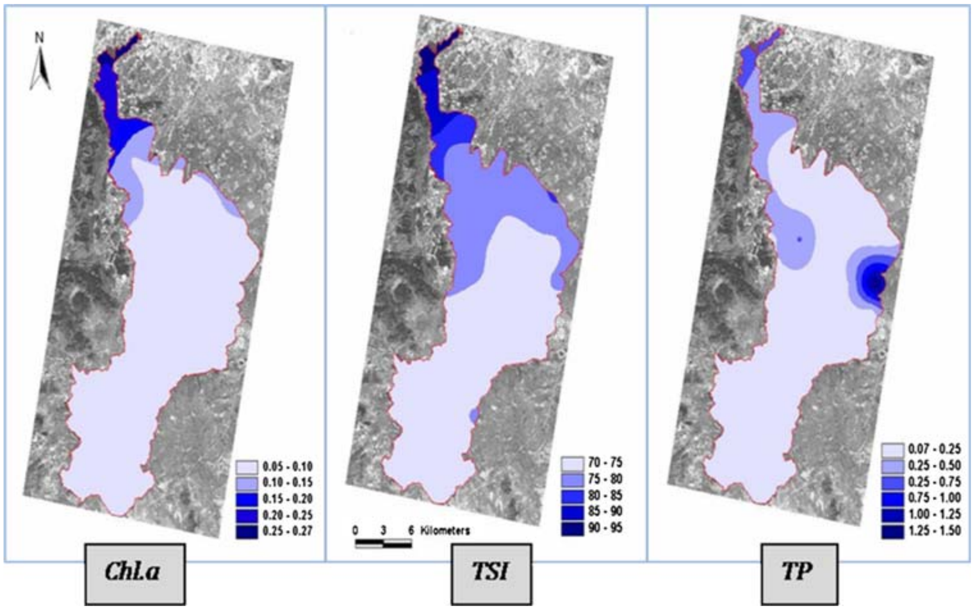

Fig. 1 Map of Chl. *a*, TSI and TP distribution in Lake Dianchi in 2001–2002(TN/TP: mg/L; TSI: dimensionless)

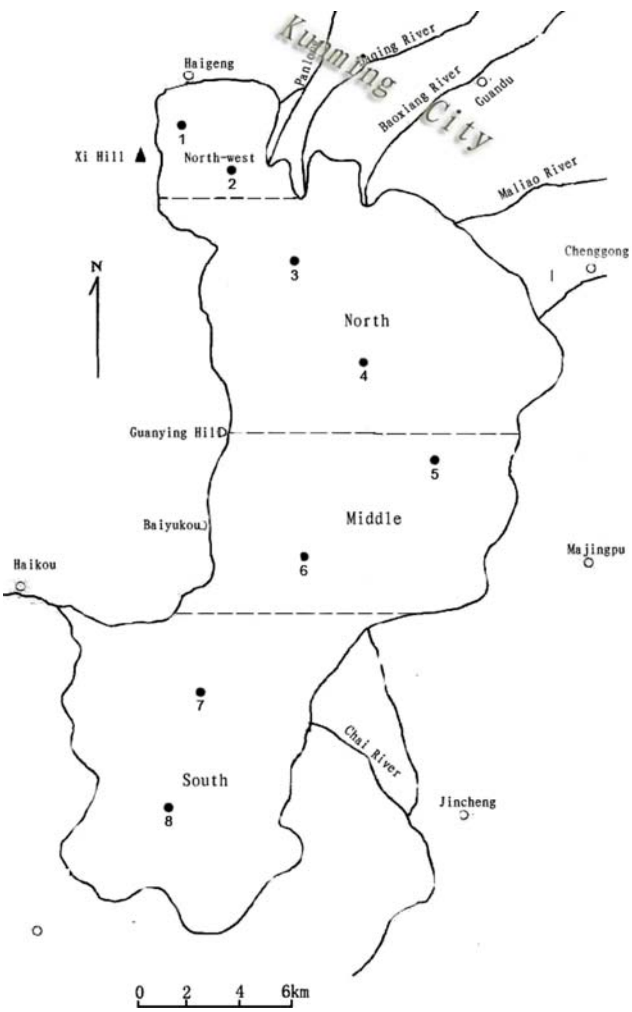

Fig. 2 Map of Lake Dianchi showing the positions of the sampling sites

extraction scheme (Hieltjes and Lijklema 1980). The samples were subjected to sequential chemical extraction with 1 M NH_4Cl, 1 M NaOH and 0.5 M HCl. At each step, the extract was centrifuged at 4000 rpm for 15 min and the soluble reactive phosphorus (SRP) in the supernatant determined as the extractable phosphorus by the molybdenum blue/ascorbic acid method (APHA 1995). However in the NaOH extraction step, the non-soluble reactive phosphorus (NRP) was determined as the difference between TP of the supernatant and the soluble reactive phosphorus. All the concentrations of phosphorus in the sediment and suspended matter were expressed based on the dry mass at 80°C (unit: mg P/g dm).

Phosphorus fractionation

According to the above extraction process, the phosphorus species are fractionated into labile P (NH_4Cl), metal oxide bound P (NaOH-SRP), Organic P (NaOH-NRP) and calcium bound P (HCl-P).

NH_4Cl-P: It is the phosphorus loosely adsorbed to the surface of Fe and $CaCO_3$ and soluble reactive phosphorus in interstitial water (Gonsiorczyk et al. 2001), and phosphorus leachable from decaying cells of bacterial biomass in deposited phytodetrital aggregates (Pettersson 2001). This is the result of weak adsorption, and in general is immediately available P (Gonsiorczyk et al. 2001).

NaOH-SRP: It is the phosphorus bound to metal oxides and exchangeable against OH^- ions, as well as inorganic phosphorus compounds soluble in bases (Hupfer et al. 1995). Phosphorus will be released from sediment under conditions of high pH, due to hydroxide ions substitution for orthophosphate (Boström and Pettersson 1982; Lijklema

1977), as well as hydroxide competing with phosphate ions for sorption sites on Fe-hydroxides. In the study of AAP (algal available phosphorus), NaOH is often used to directly extract from the sediment and the reactive phosphorus in the extraction is regarded as AAP (Butkus et al. 1988; Dorich et al. 1980). Hence, the NaOH-SRP fraction is also regarded as the estimation of AAP.

NaOH-NRP: This is the non-reactive P part in the extraction by NaOH, and commonly described as organic P (Hieltjes and Lijklema 1980), including poly-P, organic P in detritus, P bound to humic compounds (Hupfer et al. 1995).

HCl-P: This is the phosphorus bound to carbonates, apatite phosphorus and traces of hydrolyzed organic phosphorus. It is a relatively stable fraction of sedimentary origin and contributes to the permanent burial of P in sediments (Boström et al. 1988; Kaiserli et al. 2002).

Statistical

Because the environmental variables do not follow a normal distribution, the nonparametric tests, Kruskal–Wallis (*K–Z*) test and Spearman rank order correlations, were applied in the paper. K-means clustering was used in this study. All statistical analysis was performed using Minitab 15 Software package.

Results and discussion

LOI of suspended matter ranged from 39 to 97% and was much higher than that of the sediment which ranged from 5 to 13%. There were great differences between the absolute concentrations as well as the relative proportions of the TP fraction of the suspended matter and the sediment. In the suspended matter, the rank order of the mean concentrations of P-fractions on four occasions was NaOH-NRP > HCl-P > NaOH-SRP > NH_4Cl-P except for site 1where the rank order in the sediment was HCl-P > NaOH-SRP > NaOH-NRP > NH_4Cl-P except that NaOH-SRP concentrations of the fifth and the sixth sites were higher than that of HCl-P (See Figs. 3, 4, 5, 6). A separate discussion of P-fractions about suspended matter or sediment is given below

Suspended matter in Lake Dianchi

Figure 3 shows that the concentrations of TP, Chl. *a*, NaOH-NRP in the northwest (first and second) were the highest, followed by those in the middle and south. In fact, the highest concentrations of P-fractions, LOI and Chl. *a* were in the first site. In Lake Dianchi, the northwest is adjacent to Kunming City and subject to the most concentrated pollution, which appear to be responsible for the most serious water pollution in the area (Fang et al. 2004).

The *K–Z* test also indicated the sampling area had a significant effect on the concentrations of TP, NaOH-NRP, LOI and Chl. *a* ($P < 0.05$). Spearman Rank Order Correlations were calculated from the data used in Fig. 3. The significant correlations in Table 2 indicate that Chl. *a* is significantly correlated to TP and NaOH-NRP, although LOI was not significantly correlated to Chl. *a* despite a reduction in biomass from the northwest to the south. The data in Fig. 3 show that TP, NaOH-NRP, LOI and Chl. *a*

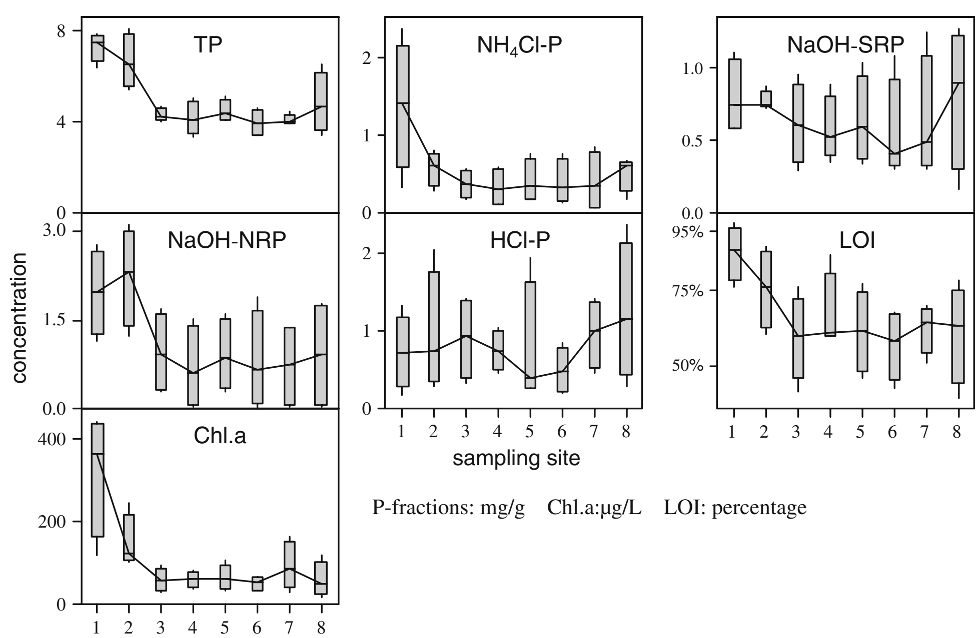

Fig. 3 The spatial distribution of the different P-fractions, LOI and Chl. *a* in the suspended matter from the eight sites in Lake Dianchi

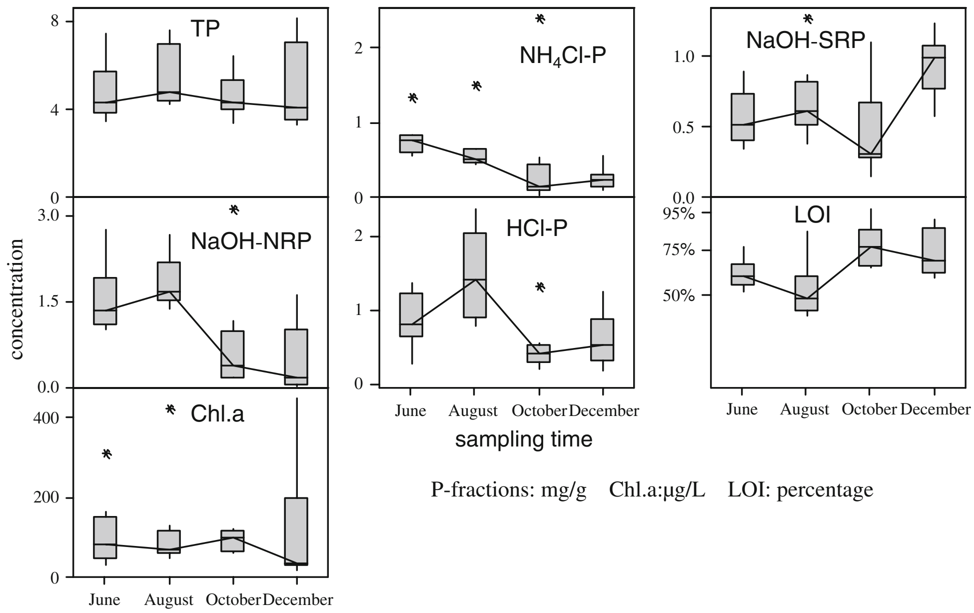

Fig. 4 The temporal-distribution of the different P-fractions, LOI and Chl. *a* in suspended matter (*asterisk* outlier)

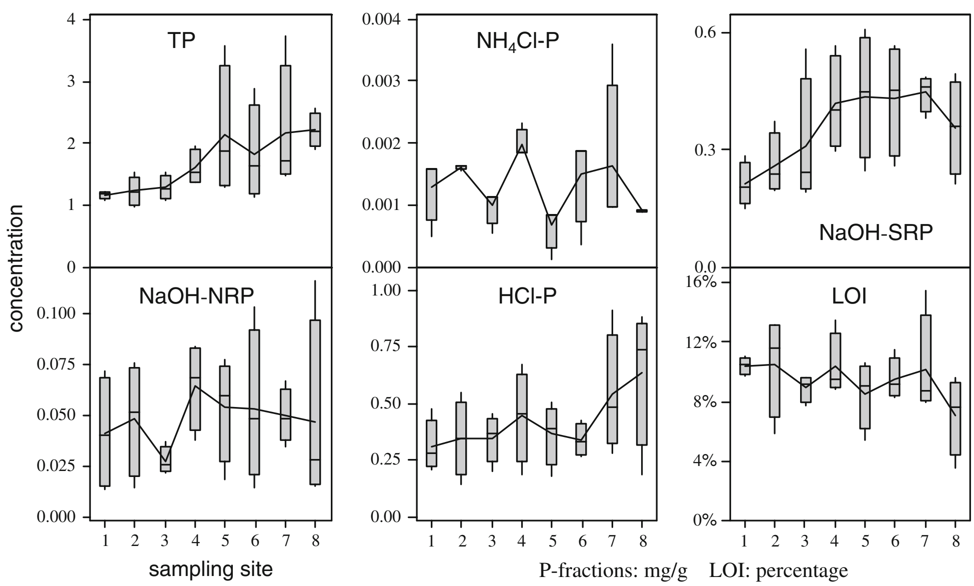

Fig. 5 The spatial distribution of the different P-fractions and LOI in the sediment from the eight sites in Lake Dianchi

had similar trends. The results from the *K–Z* test and the correlation analysis were consistent with the trends in Fig. 3. Their distribution was similar to the distributions of trophic status and the extent of cyanobacterial blooms of Lake Dianchi. NaOH-SRP and HCL-P mainly contain inorganic phosphorus, while NaOH-NRP mainly means organic P including P in cyanobacteria. It is speculated that cyanobacterial blooms can have little effect on them. All these show that the cyanobacterial bloom can be the main source of phosphorus, especially organic phosphorus (NaOH-NRP), but not organic matter. Because Chl. *a* reflects the biomass of cyanobacteria, it further indicates that organic suspended matter cannot contain much phosphorus besides cyanobacteria. Another phenomenon is that NH_4Cl-P had a positive correlation with NaOH-NRP and HCl-P, which shows that organism and Ca compounds both have intensive capacity to absorb phosphate or, a high NaOH-NRP always means there are a great many organisms. In addition LOI had a negative correlation with HCl-P.

The temporal-distribution of the suspended matter in Lake Dianchi

Figure 4 shows that the concentration range of Chl. *a* was mainly between 10 and 150 µg/L. The *K–Z* test also indicated that the sampling time had a significant effect on the concentrations of NaOH-NRP, NaOH-SPR, NH_4Cl-P,

Fig. 6 The temporal-distribution of the different P-fractions, LOI and Chl. *a* in sediment (*asterisk* outlier)

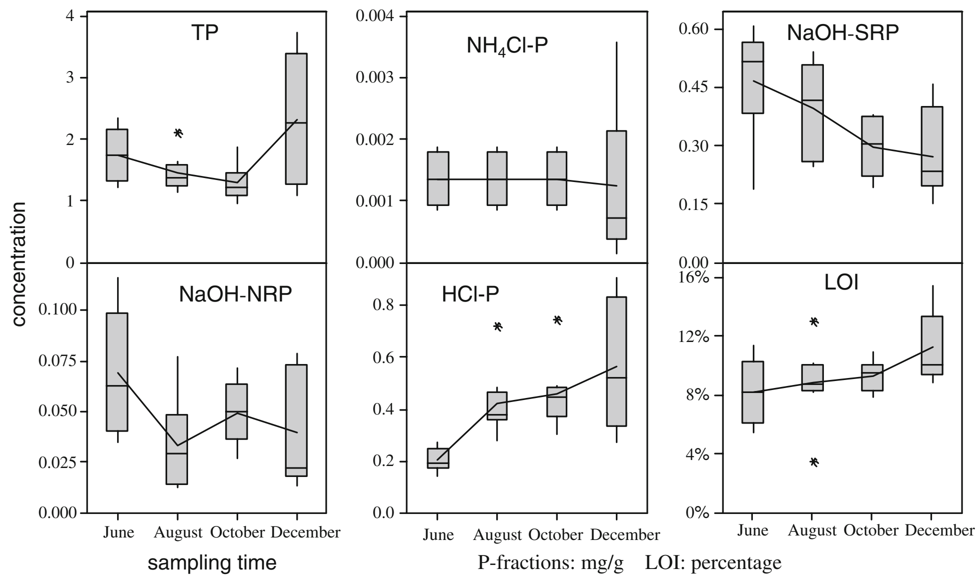

Table 2 Spearman rank order correlations and *K*–*Z* test results in the suspended matter

Correlations	TP	NH_4Cl-P	NaOH-SRP	NaOH-NRP	HCl-P	LOI	Chl. *a*
TP	1.00	0.36	0.30	*0.66*	0.17	0.22	*0.52*
NH_4Cl-P	0.36	1.00	0.20	*0.66*	*0.47*	−0.18	0.31
NaOH-SRP	0.30	0.20	1.00	0.02	0.41	0.06	−0.27
NaOH-NRP	*0.66*	*0.66*	0.02	1.00	0.41	−0.22	*0.52*
HCl-P	0.17	*0.47*	0.41	0.41	1.00	*−0.50*	−0.25
LOI	0.22	−0.18	0.06	−0.22	*−0.50*	1.00	0.38
Chl. *a*	*0.52*	0.31	−0.27	*0.52*	−0.25	0.38	1.00
K–*Z* test (*P*-value)	0.001	0.086	0.311	0.020	0.316	0.017	0.002

the values in italics mean that the correlations are significant at $P < 0.01$ or $P < 0.05$

HCl-P and LOI ($P < 0.05$). No effect was found on TP and Chl. *a*. Again it shows that TP in Lake Dianchi was closely related to Chl. *a*. Concentration of NH_4Cl-P was gradually dropping from the first to the last sample. NaOH-NRP and HCl-P in October and December were lower than in June and August, but LOI was on the contrary. NH_4Cl-P represents a fully exchangeable and therefore bioavailable phase, and then it is immediately available phosphorus. But for the other P-fractions, the bioavailability depends on geochemical transformation and on the time allowed for diagenesis (Pacini and Gächter 1999). The decline of NH_4Cl-P means a reduction of immediately available phosphorus due to the assimilation of cyanobacteria. By course the decline was attributed to another cause, namely the elevated bacterial biomass and activity can contribute to the high proportions of labile P in suspended matter and settling particles in summer (Pettersson 2001). NaOH-SRP was highest on the fourth sampling date, which can be related to the transformation of redox-sensitive P (Hu et al. 2007).

Sediment in Lake Dianchi

Figures 3 and 5 show that the spatial distribution of each phosphorus fraction in the sediments was different to the corresponding distribution in the suspended matter. The distribution and concentrations of TP and P-fractions were similar to what was reported by Hu et al. (2007). NaOH-NRP and NH_4Cl-P were much lower than that in the suspended matter in the corresponding area. TP was low in the northwest and slightly increased towards the south. But it is opposite to the corresponding distribution pattern of suspended matter. The high concentration of NaOH-SRP appeared near the south. The *K*–*Z* test indicated that TP and NaOH-SRP were significantly different in four sampling areas ($P < 0.05$). The correlation analysis (Table 3) also showed that both were negatively related to Chl. *a* ($P < 0.05$).

NaOH-SRP is regarded as potentially algae-available phosphorus. Lower concentrations can be due to cyanobacteria assimilating this form of phosphorus, so where

Table 3 Spearman Rank Order Correlations and *K–Z* test in the sediment

Correlations	TP	NH_4Cl-P	NaOH-SRP	NaOH-NRP	HCl-P	LOI	Chl. *a*
TP	1.00	−0.18	*0.48*	0.10	0.23	−0.16	*−0.6*
NH_4Cl-P	−0.18	1.00	0.22	0.43	0.02	0.36	0.04
NaOH-SRP	*0.48*	0.22	1.00	0.40	−0.22	*−0.46*	*−0.35*
NaOH-NRP	0.10	0.43	0.40	1.00	−0.13	0.09	0.09
HCl-P	0.23	0.02	−0.22	−0.13	1.00	0.33	−0.24
LOI	−0.16	0.36	*−0.46*	0.09	0.33	1.00	0.10
Chl. *a*	*−0.6*	0.04	*−0.35*	−0.09	−0.24	0.10	1

the values in italics mean that the correlations are significant at $P < 0.01$ or $P < 0.05$

there was the higher concentration of Chl. *a* there was the lower concentration of NaOH-SRP. The decrease of TP from the north to the south can partly be due to the assimilation and the autogenous environment (Hu et al. 2007). HCl-P is a relatively stable composition in sediment. The concentrations of the preceding six sites were similar, but the concentrations of seventh and eighth site were much higher than other sites, which can also be by virtue of phosphorus mineral (Xia et al. 2002). NaOH-SRP was significantly correlated to TP, and the increase in NaOH-SRP can lead to the increase of TP. NaOH-SRP was negatively correlated to LOI. The quick degradation and mineralization of organic matter leads to the lower concentration of LOI, and can also induce the phosphorus release from organisms.

The *K–Z* test indicated that the sampling time had a significant effect on NaOH-SRP and HCl-P ($P < 0.05$), but the other P-fractions and LOI were not significantly different during the four sampling times. Figure 6 shows that NH_4Cl-P and NaOH-NRP were lower than the other P-fractions. NaOH-NRP on the first sampling date was a little higher than the other three times. NaOH-SRP gradually decreased from the first time to the fourth time, and NaOH-SRP is regarded as potentially available phosphorus. The decrease in NaOH-SRP shows that NaOH-SRP in sediment can be a nutrient released from sediment to water (Zhou et al. 2001).

Comparison of the distributions

The data of the suspended matter and the sediment were classified into two separate sets by the K-means clustering method, which show there was a distinct difference between the phosphorus characteristics in the sediment and that in the suspended matter.

As a whole, the concentrations of the phosphorus fractions and LOI in suspended matter were higher than the corresponding concentrations in sediment. Similar results were reported by Pettersson (2001). Due to wind-induced turbulence, sediment particles might be resuspended into the water body. Slowly settling particles including phytoplankton, organic detritus and light minerals, remain on average longer in the free water column than heavier particles. When the concentration of phosphorus and LOI are expressed on the basis of dry mass, the concentration of phosphorus in suspended matter should be higher. In Lake Dianchi, The 80% of TP in sediment was lower than 2 mg/g and the maximum was less than 3.5 mg/g. However, the concentration of phosphorus in cyanobacteria is approximately 4 mg/g dw (Shen et al. 2004), so TP of suspended matter was much higher than that in sediment in this study. The spatial distributions of TP in sediment and suspended matter are opposite to each other, and the differences can be interpreted according to the distribution of Chl. *a*. The scale of the cyanobacterial blooms is greater than in the water body, which has a higher TP. At the same time, because cyanobacteria take up P, there can be lower concentrations in the sediment. In the central of Lake Dianchi there are few macrophytes, and thus the main origin of organic matter is the living cyanobacteria and debris. Cyanobacteria are the main living organism in the water so there is a higher concentration of LOI in water than in sediment. The concentrations of LOI in sediment and in suspended matter were both falling from north to south. In view of the state of cyanobacterial blooms, it is reasonable.

The content of NaOH-SRP and HCl-P in both sediment and suspended matter was closer than that of the other P-fractions. The HCl-P and NaOH-SRP fractions mainly consist of some metal ions or metal phosphorus compounds, but phosphorus in cyanobacterial blooms is mainly organic phosphorus. Compared with TP, NH_4Cl, NaOH-P and LOI, their distributions are more uniform whether in sediment or in suspended matter. Considering the sequential P extraction as the method to trace sediment source (Pacini and Gächter 1999), it might be speculated that the NaOH-SRP and HCl-P mainly derive from the particles resuspended from the sediment, while NaOH-NRP is P in cyanobacteria.

Figure 7 shows more information on the relative contribution of each P-fraction to TP. The concentration of each fraction was the mean value at the same site. According to Figs. 3 and 5, it can be seen that all P-fractions in suspended matter were higher than the corresponding P-fractions in sediment. Figure 7 showed that

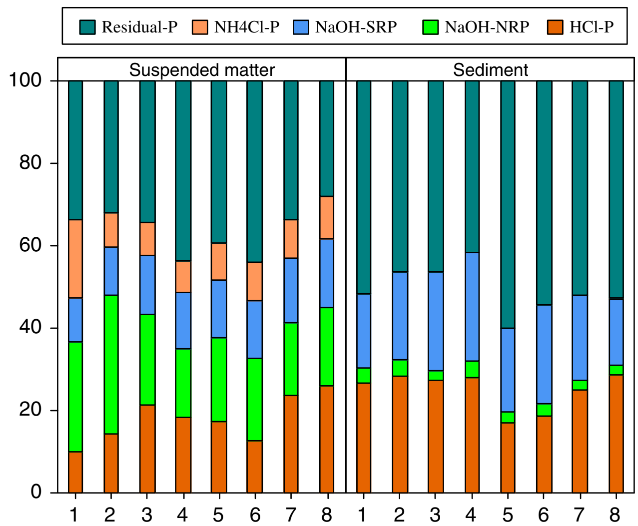

Fig. 7 The relative contribution of each P-fraction to TP in sediment and suspended matter for eight different sampling sites (arithmetic mean of four different sampling dates from June 2004 to December 2004). Remark: residual-P = TP−(HCl-P + NaOH-SRP + NaOH-SRP + NH4Cl-P)

the relative contributions of NH_4Cl and NaOH-NRP to TP in suspended matter still were higher than that in sediment, but NaOH-SRP and HCl-P were opposite. The relative contribution of NaOH-SRP to TP in suspended matter being lower than that in sediment implies that the potentially available phosphorus was dropping from the lake water to the sediment. In suspended matter, NH_4Cl-P ranged from 0.2 to 0.8 mg/g dm with a maximum close to 2.4 mg/g dm (at first site). However, in sediment all NH_4Cl-P did not exceed 0.004 mg/g dm. Analogously NaOH-NRP was much lower in the sediment than in the suspended matter. Pettersson's study (Pettersson 2001) indicates that the appearance and sedimentation of pelagic phytoplankton, bacteria and organic detritus primarily affect the organic P (NaOH-NRP) and labile P (NH_4Cl-P) fractions. This coincides with low allochtonous input and less resuspended material (Weyhenmeyer 1996, 1999). Hence in Pettersson's study, the decrease in labile phosphorus and organic phosphorus from suspended matter to sediment is ascribed to the effect of phosphorus leakage and mineralization. But in Lake Dianchi, which is a shallow lake different from Lake Erken, the turbulence created by wind is more important. The increase in the concentration of NH_4Cl-P can be strongly related to the action. The higher concentration of NH_4Cl-P indicates that the sorption capacity of suspended matter to adsorb inorganic phosphorus is much higher than that of sediment particles. After resuspension, particle sizes are reduced due to mechanical shear stress and thus the surface areas are increased. The increase of surface potential energy contributes to the enhancement of the sorption capacity in the light of the thermodynamics theory. An investigation on Lake Arresø in Denmark resuspension increases the nutrient concentration in the water 20–30 times (Søndergaard et al. 1992). In Lake Dianchi the concentration of phosphorus in the porewater is much higher than that of the overlying water (Hu et al. 2005). When dissolved phosphorus is released into the water body by sediment resuspension due to wind activities or the diffusion of dissolved phosphorus in porewater, the sorption of the suspended particles maintain the concentration of dissolved phosphate relatively stable in the water and make the concentration of NH_4Cl-P higher in the water. In fact it is as a result of phosphate buffer mechanism reported by Froelich (1988).

Conclusion

In Lake Dianchi, cyanobacterial blooms can strongly affect the spatio-temporal-distribution of phosphorus in water and sediment.

In this study, TP and NaOH-NRP in suspended matter had a positive correlation with Chl. *a*. The organic phosphorus in suspended matter might mainly consist of phosphorus in cyanobacteria.

Inorganic phosphorus (NaOH-SRP and HCl-P) is derived from sediment. Concerning NH_4Cl-P and NaOH-SRP, their change in the absolute concentrations and the relative contribution to TP indicated that there was a stronger mineralization of suspended matter than of sediment.

Cyanobacterial blooms can promote the transformation among P-fractions. Studying the relative contribution of NH_4Cl-P to TP, it can speculated that NH_4Cl-P is more important for suspended matter and can be a phosphorus pool with buffer capacity for the lake water.

Acknowledgment This research work was supported by the National Basic Research Project of China 2009CB118705.

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